CANMET

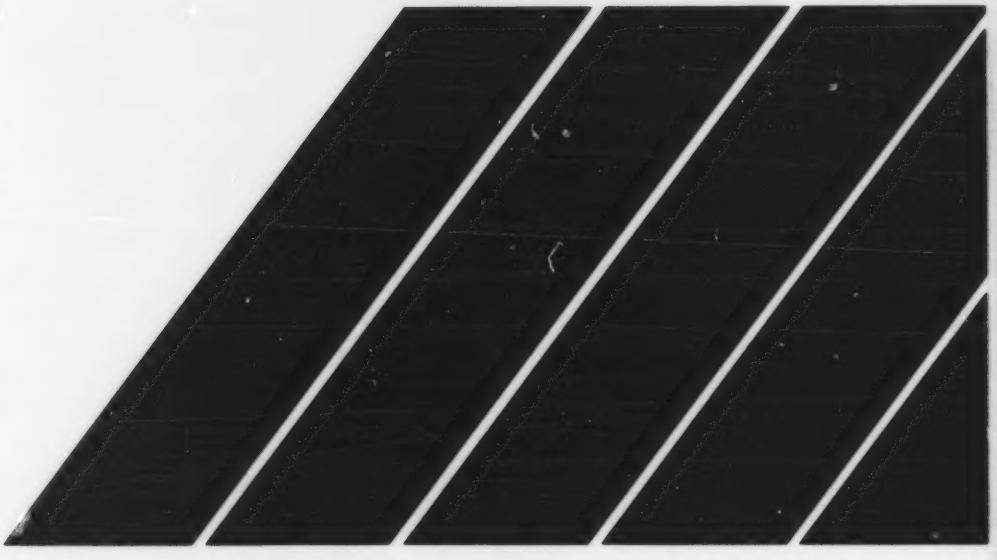
Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

Efficiency and Alternative Energy Technology Branch

Direction de la technologie de l'efficacité énergétique et des énergies de remplacement

FURTHER DEVELOPMENT OF ELECTROPLATED CdTe-BASED PHOTOVOLTAIC CELLS



Energy, Mines and Resources Canada

Énergie, Mines et Ressources Canada

Canada

THE ENERGY OF OUR RESOURCES · THE POWER OF OUR IDEAS

L'ENERGIE DE NOS RESSOURCES · NOTRE FORCE CRÉATRICE

91-01226/

FURTHER DEVELOPMENT OF ELECTROPLATED CdTe-BASED PHOTOVOLTAIC CELLS

PREPARED FOR:

Efficiency and Alternative Energy Technology Branch
Energy, Mines and Resources Canada
Ottawa, Ont.
DSS Contract No. 23283-7-6233
February, 1990

PREPARED BY:

A.D. Plating & Electroforming Inc.
110 Aikman Ave.
Hamilton, Ont.
L8M 1P9
(416) 523-4636

SCIENTIFIC AUTHORITY:

Jimmy Royer
Efficiency and Alternative Energy Technology Branch
Energy, Mines and Resources Canada
580 Booth Street
Ottawa, Ont.
K1A 0E4

40 pp

MICRO

CITATION

A.D. Plating & Electroforming Inc. Further Development of Electroplated CdTe-Based Photovoltaic Cells. DSS Contract No. 23283-7-6233. Efficiency and Alternative Energy Technology Branch, Energy, Mines and Resources Canada, Ottawa, Ontario. 1990 (33 pp.)

Copies of this report may be obtained through the following:

Efficiency and Alternative Energy Technology Branch
Energy, Mines and Resources Canada
580 Booth Street, 7th Floor
Ottawa, Ont.
K1A 0E4

or

Document Delivery Service
Library and Documentation Services Division
CANMET
Energy, Mines and Resources Canada
562 Booth Street
Ottawa, Ont.
K1A 0G1

DISCLAIMER

This report is distributed for informational purposes only and does not necessarily reflect the views of the Government of Canada nor constitute an endorsement of any commercial product or person. Neither Canada nor its ministers, officers, employees or agents makes any warranty in respect to this report or assumes any liability arising out of this report.

NOTE

Funding for this project was provided by the Office of Energy Research and Development, Energy, Mines and Resources Canada.

© Minister of Supply & Services Canada 1990
Catalogue No. M91-7/117-1990E
ISBN. 0-662-18163-8

ABSTRACT

Over the last two years A. D. Plating has gained substantial experience in making CdTe based polycrystalline solar cells.

A pilot station for the electrodeposition of CdTe was built. We were able to produce on this pilot station, with industrial grade chemicals, a 5.5 % efficiency CdS/CdTe device and 2% efficiency MIS device.

A detailed description of the processes, by which a good CdTe based solar cell can be obtained, is part of this report.

TABLE OF CONTENTS

	Page
Abstract	iv
Executive Summary	v
Résumé	vi
Introduction	1
1. ELECTRODEPOSITION OF CdTe	2
1.1 Electrode Kinetics	3
1.2 Tellurium Replenishment	7
1.3 Substrates	8
1.4 Pilot Station	11
2. PREPARATION OF CdS	14
2.1 Electrodeposition of CdS	14
2.2 Evaporation in Vacuum of CdS	14
3. Au/CdTe/Ni MIS SOLAR CELL	16
3.1 Cell Configuration and Fabrication	16
3.2 Device Evaluation	20
4. CdS/CdTe CELLS	23
4.1 CdS/CdTe Cell Fabrication and Evaluation	23
5. CONCLUSION	28
6. RECOMMENDATION	29
APPENDIX	

SUMMARY

In the last four years, A.D. Plating dedicated most of its talent and effort to develop a thin film polycrystalline solar cell. This effort was encouraged by the fact that this type of device has become, in recent years, the leading contender.

There were two main objectives:
1) The development of a metal-insulator-semiconductor cell having an area of 150 sq.cm. and an efficiency of at least 5%.

2) The development of a CdS/CdTe heterojunction cell having an area of 75 sq.cm. and an efficiency greater than 1%.

Encouraged by former results, we built a pilot station for producing large area CdTe films by electrodeposition. This was above our contractual obligation, and reflected our confidence in the process. Unfortunately, a subtle blend of conditions produced problems which eluded us for many months. We spent much more time and resources than expected making the pilot station work .

Still, with all the difficulties, we were able to produce on the pilot station, with industrial grade chemicals, MIS devices with an efficiency in excess to 2%. In our understanding,this is a substantial realisation.

We started work on objective (2) very late and with little resources. We obtained CdS/CdTe devices with efficiency five times better than expected, but the labourious task of ensuring uniformity on a very large area could not be completed in time and the tested cells are 0.33 sq.cm. instead of 75 sq.cm. Nothing suggests, at this time, that we will have problems scaling up the area of the cells.

Probable record high, short circuit current was obtained but the cell did not survive some rather crude manipulation for a documented performance.

A detailed description of the processes, by which a good CdTe based solar cell can be obtained, is part of this report.

The process is difficult. Subtle changes in preparation have dramatic effect on performances. The most difficult time in learning to produce thin film polycrystalline solar cells has passed, but one or two years of R&D work is still necessary to improve the yield, to increase the efficiency, and to produce submodules.

RÉSUMÉ

Au cours des quatre dernières années, A.D. Plating a consacré la plus grande part de ses ressources et de ses efforts à développer une pile solaire polycristalline à couche mince. Ces travaux étaient soutenus par le fait que ce type de dispositif représentait depuis quelques années la solution de rechange la plus prometteuse.

Deux principaux objectifs étaient visés :

1) le développement d'une pile à métal-isolant-semiconducteur présentant une surface de 150 cm^2 et un rendement d'au moins 5 %, et

2) le développement d'une pile à hétérojonction CdS/CdTe présentant une surface de 75 cm^2 et un rendement supérieur à 1 %.

Encouragés par des résultats antérieurs, nous avons fabriqué un poste pilot permettant de produire des couches de CdTe de grande surface selon le processus d'électrodéposition. Ces travaux allaient au-delà de nos obligations contractuelles et reflétaient notre confiance envers le processus. Malheureusement, un délicat mélange de diverses conditions a créé des problèmes qui nous ont fait obstacle durant plusieurs mois. Nous avons consacré beaucoup plus de temps et de ressources que prévu à faire fonctionner le poste pilote.

Malgré toutes ces difficultés, nous avons néanmoins réussi à produire des dispositifs dont le rendement excédait 2 % en utilisant le poste pilote et des produits chimiques de qualité industrielle. A notre avis, il s'agit là d'une réalisation notable.

Nous avons entrepris les travaux de notre deuxième objectif avec beaucoup de retard et peu de ressources. Nous avons obtenu des dispositifs au CdS/CdTe offrant un rendement cinq fois plus élevé que prévu, mais les laborieux travaux d'uniformisation sur très grande surface n'ont pu se terminer à temps et les piles vérifiées sont de 0.33 cm^2 plutôt que de 75 cm^2. Pour le moment, rien ne laisse prévoir que nous aurons des problèmes à augmenter la surface des piles.

Un courant de court-circuit atteignant probablement une intensité record a été obtenu, mais la pile n'a pu résister aux manipulations plutôt rigoureuses qui auraient permis d'en documenter les performances.

Une description détaillée du processus de fabrication d'une bonne pile solaire au CdTe est incluse dans le rapport.

Le processus est exigeant. De légères modifications des

préparatifs ont un effet considérable sur le rendement. La période la plus difficile d'apprentissage du processus de fabrication des piles solaires polycristallines à couche mince est maintenant terminée, mais une ou deux années de recherche et développement sont encore nécessaires pour améliorer la production, augmenter le rendement et produire des sous-modules.

INTRODUCTION

For years polycrystalline thin film solar cells trailed the amorphous silicon device in efficiency. In 1989, this situation was reversed and the highest efficiency of 14.1% for thin film structure was achieved with CuInSe. CdTe have attained 12.3%. Submodule efficiencies reached 11.1% for CuInSe and 7.3% for CdTe. The stability is the best and processes have the lowest cost.

In Canada, A.D. Plating is the only company which works on thin film solar cell pursuing commercial exploitation. Unfortunately, our performances are one-two years behind state-of-the-art achievements. This situation is deplorable, but considering the level of expertise reached with 10 times fewer resources than any other small R%D group involved with thin film solar cells ,we are confident that sooner or later we will be recognised as a leading group in thin film photovoltaic devices.

1.ELECTRODEPOSITION OF CADMIUM TELLURIDE

Electrodeposition of CdTe was proposed fifteen years ago as an easy to scale up, inexpensive way to produce large area solar cells. Since then, electrodeposition has been used and is constantly being improved in a few laboratories around the world who believe that this technique has advantages over many other ways of producing thin films of CdTe.

In the last few years, considerations such as waste management, and environmental effects were added to the list of advantages over other techniques.

Electrodeposition involves a very large number of interdependent parameters which can affect dramatically the electrical properties of the deposit, and in this respect makes the already difficult task of making good, inexpensive solar cells even more difficult.

Most of the theoretical and basic information necessary for a good understanding of the process of electrodepositing CdTe was summarized in a previous report. It is reproduced here in "Appendix 1".

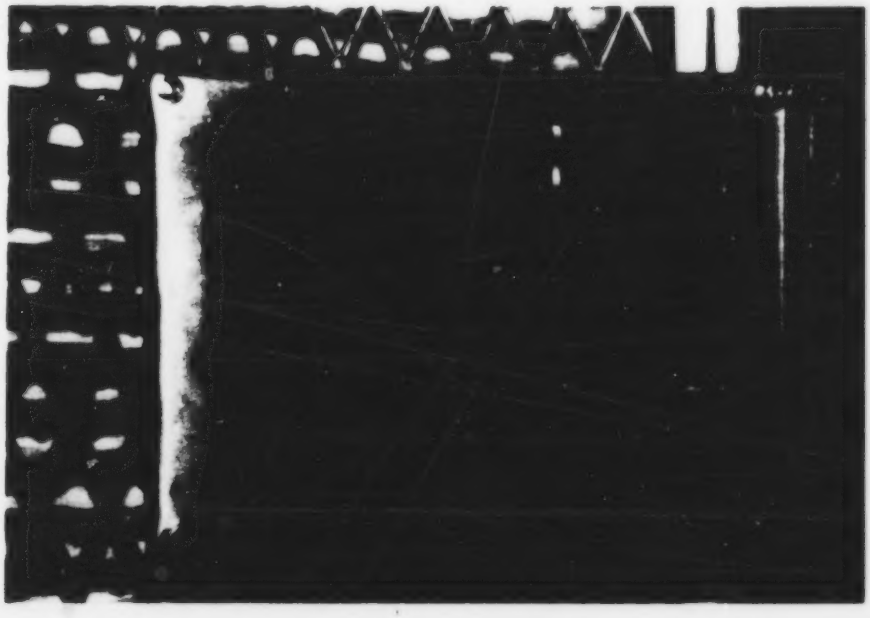


Fig. 1. A previously produced MIS CdTe based solar cell.

We started the work on this project being able to produce, in a small glass reactor and a thermal evaporation vacuum system,

Schottky barrier CdTe/Au devices of rather large areas. The cell had 1% efficiency, and a bad fill factor but was large enough to produce 100 mA. The cell has nine segments in parallel and is pictured in Fig 1. It was not easy for us to produce these cells. Everything had to run perfectly and small variations in the process induced modifications strong enough to reduce the number of well performing cells to less than one in ten. However, the cell, once produced with good yields, is very inexpensive. It could be improved dramatically by lowering the series resistance and lowering the reflection of light on top of the cell.

The tasks of the present work on electrodeposition of CdTe were:

1) To gain a better understanding of the effect of deposition conditions on the quality of the deposit.

2) To modify and improve the process to obtain better films in shorter time.

3) To build a pilot line and to gain experience in designing such an installation.

All tasks proved to be highly challenging and, despite the fact that we spent twice as much time as planned, there are still many problems to be addressed and a better understanding gained.

1.1 ELECTRODE KINETICS

The application of the Nerst equation determined that the activities of tellurium ions in solution had to be much smaller than that of cadmium ions. This condition is met without any difficulty considering that tellurium ions are provided by the slightly soluble TeO_2 and Cd ions by the very soluble $CdSO_4$.

The hydrated tellurium and cadmium ions present in the electrolyte arrives at the cathode under the influence of the imposed electrical field as well as by diffusion and convection. At the cathode, they enter the diffusion layer in which the osmotic pressure is in equilibrum with electrostatic forces. The field strength in the outer diffusion layer is not sufficient to liberate the ions from their hydrate envelope. The hydrated ions move further into the fixed double layer by diffusion where the field is approximately 10^7 v/cm and the ions were deprived of their envelope.

If the electrode potential has a value somewhere between E_{Te} and E_{Cd}, the tellurium ion passes through the double layer and is then neutralized and absorbed at the cathode surface. This ad-atom now diffuses on the cathode to a growth point and is

then incorporated into the crystal lattice of the cathode as can be seen in Fig. 2. The Cd dehydrated ion, in our opinion, migrates within the outer zone of the double layer to a point opposite the occupied Te site . From this point, the cadmium ion passes through the double layer, is neutralised and deposits on the cathode.

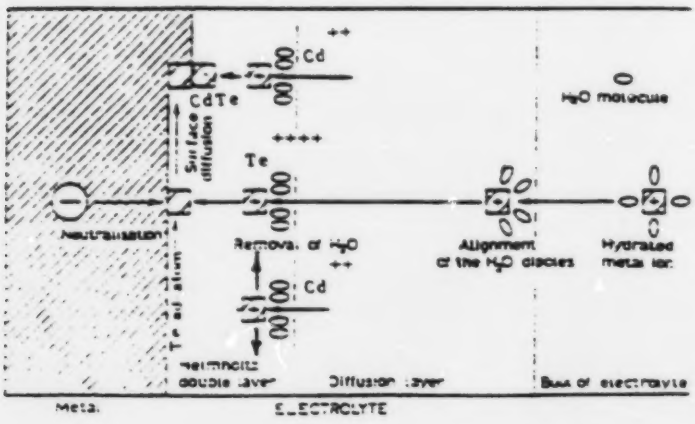


Fig. 2. Schematic representation of the mechanism of cathodic codeposition of cadmium and tellurium.

Cd cannot deposit at an electrode potential below E_{Cd} unless a Te atom is incorporated into the lattice. Cd deposition will occur at a potential less negative than Eo by using the increment in Gibbs free energy when CdTe forms. If the concentration of the Cd ions are high at the edge of the double layer, as soon as a tellurium ad-atom has taken its stable place, it will trigger the reduction of a cadmium atom with formation of CdTe.

The mechanism described above is rather complicated but the explanation of the numerous peculiarities of the deposits, obtained in different runs, in conditions almost identical, requires a complete understanding of the electrode process.

On top of all the difficulties arising from the interplay of the very large number of parameters, (in consideration of our goals) we had to work with industrial grade chemicals. This approach is a serious drawback, at least for the time being, and instead of

reporting state-of-the-art performances, we still agonize with rather low efficiencies. The good thing about this is that, for industrial production purposes, our competition will have to start again but we will be well prepared for it.

Once the composition of the bath is correct; the temperature stable; the electrolyte agitation very uniform; impurities at an extreme low level; and no contamination occurring; a high quality,

Fig. 3. A cut through an CdTe deposit on nickel plated brass substrate.

uniform layer of CdTe will be deposited at a current density of 0.1-0.5 mA-cm square. Figure 3 and 4 represent one such film. Fig. 3 shows a portion of a brass substrate, followed by an almost amorphous layer of electrodeposited nickel on which approximately two microns thick of CdTe is showing. Fig.4 represents the same film at a higher magnification. The topography of the surface is evident. Very little morphology is shown. A columnar growth can be suggested.

At electrode potential close to that necessary for cadmium deposition, dendrites have the tendency to form. This is a feature which might be characteristic only of our composition. However, it is important to understand its origin because the very good and very bad deposits have this in common. A deposit which is produced at high current density will be n type, faster growing and will incorporate fewer impurities. Practice shows these films are of better quality. If the bath is contaminated, dendrites form at a lower potential and their aspect is slightly

different.

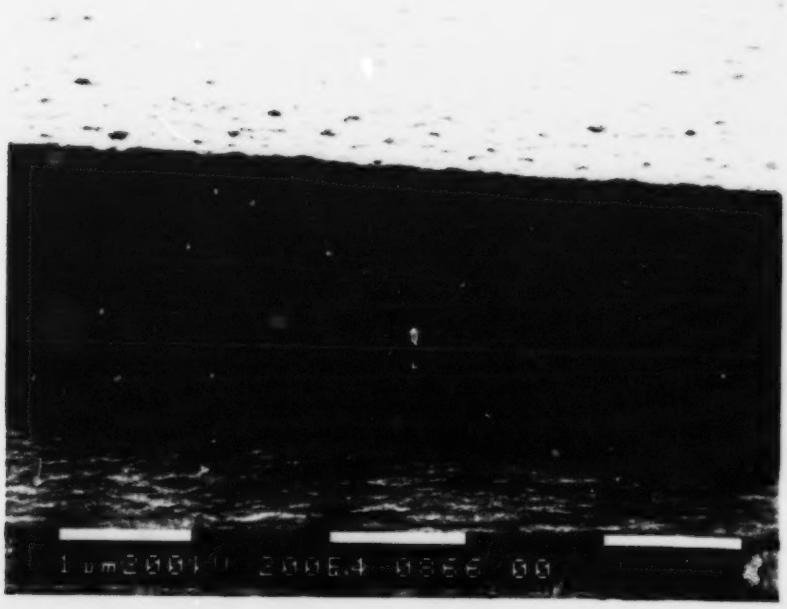


Fig. 4. Same film as in previous picture at 20,000 times magnification.

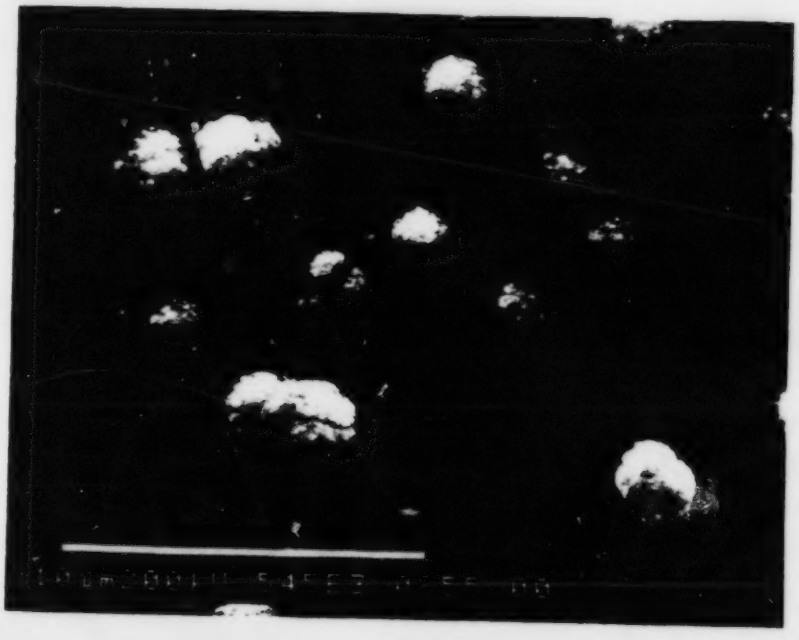


Fig. 5. CdTe nodules in high current density areas.

The formation of dendrites starts on CdTe nodules which appear randomly in areas of high current density. The nodules are pictured in figure 5.They penetrate the Helmholtz diffusion layer toward tellurium-rich electrolyte and there they grow much faster as dendritic formations.

1.2 TELLURIUM IONS REPLENISHMENT

In our previous work the source of tellurium atoms was TeO_2 which is slightly soluble in water. The oxide was dispersed as a suspension in the electrolyte,insuring as high a concentration as possible of Te^{4+}. In this way, the concentration of tellurium ions depends only on temperature but some particles could be incorporated in the deposit creating unacceptable unhomogenieties. To solve this problem, a small recirculation system was built in which a polypropylene filter retained the tellurium oxide particles without diminishing the concentration of tellurium ions. The flow of warm electrolyte through the filter should replenish the tellurium contained as tellurous acid in solution. This system, in which the

Fig. 6. Large substrate with CdTe film forming only where replenished electrolyte hits the cathode.

electrolyte was rich in tellurium at the outlet of the recirculation system made the effect of convection increase dramatically. Many "electrolyte agitation systems" were designed in which the inflowing replenished electrolyte was better and better distributed on the surface of the cathode. However, thickness uniformity is a problem in this case and complicates, unexpectedly, any scale up tentatives. Figure 6 represents a CdTe film grown with the electrolyte injected toward the substrate in a poorly designed electrolyte agitation system. Practically the electrolyte is depleted of its tellurium content before reaching far and the CdTe film is discontinued.

Anodes made of tellurium can be used as a source of tellurium ions. They are usually set in parallel with cadmium anodes and are switched on only a fraction of the plating time so their concentration in solution can be controlled. However, the anode processes are not completely understood and everybody has different "designs" for the anodes.

Initially we used graphite bars in which we bored small holes to hold the tellurium shot. This arrangement was abandoned because tellurium shot often fell out of their housing and most importantly because the graphite bars could be a source of contamination.

At present, we use as anodes large, high purity tellurium chunks wrapped in platinum wire and hung from a graphite bar to insure as uniform an electric field as possible. The ratio of the anode/cathode area has to be no more than 0.5.

1.3. SUBSTRATES.

The cost and physical properties of the substrate are very important factors in considering which solar cell system is suitable for terrestrial application. The substrate has to be inexpensive, has to have a very good corrosion resistance, and has to blend favorably with the other thin film material used in producing high efficiency solar cells. In our particular case, the substrate has to have a matching thermal expansion coefficient with cadmium telluride, has to be completely inert while in the reactor, has to insure a good adherency of cadmium telluride, and has to withstand processing temperatures of up to 400 C.

We thoroughly investigated the nickel substrate and indium tin oxide coated borosilicate glass. Nickel was our initial choice because it was handy, it has good corrosion resistance, it can be used as a plating on steel or brass plates and mostly because of our expertise with this material.

NICKEL

We used Steel plates 200 cm^2, brass plates 75 cm^2 and 3000cm^2 electroformed nickel. For the 75 cm^2. substrates a complete set of masks were made and a single cell as depicted in figure 7 were produced. The steel nickel plated substrates were considered because those substrates are the most inexpensive and easy to prepare for electrodeposition. No appreciable iron contamination was noted. However, brass was used routinely because steel was rather harder to keep rust free and less handy for daily use. The nickel plated substrate was introduced in the CdTe electroplating bath attached and held by the copper wire with which they were nickel plated. In this way a parasite electrode potential was not created and the cathode processes were not complicated.

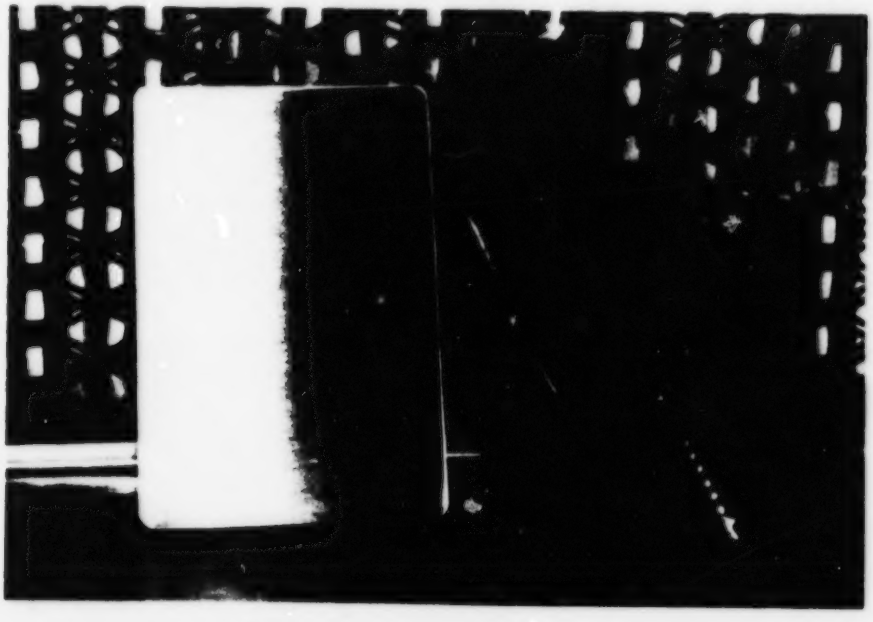


Fig.7. 45.84 cm^2 .: brass substrate and flexible electroformed nickel substrate mostly used for the MIS cells.

The electroformed nickel substrate was produced by electrodepositing nickel on a stainless steel holder and introduced in the CdTe bath on this holder. Once CdTe deposited, the nickel can be pulled off the holder and a very light, flexible solar cell can be obtained. If the CdTe film is less than 1.5 microns thick, no piling will occur during the heat treatment and flexing or bending the substrate will not make the semiconductor film crack or change its electrical properties.

The nickel has a much larger thermal expansion coefficent than cadmium telluride. This mismatch has a dramatic influence during

the thermal treatment. If CdTe is thick or the nickel surface is passivated, the whole CdTe deposit can dust off or small circular areas will break loose. This limits the thickness of CdTe to 2.5 microns. Above this thickness, pinholes will develop during annealing and the completed device will present a very low shunt resistance.

The above limitation is hard to deal with in the development phase but once good control and practice is gained, 2.5 microns thick CdTe is thick enough and we do not think this matter is a major concern.

Nickel surface passivates in seconds and molecular adherence is difficult to obtain. The surface can be reactivated by a cathodic treatment in a sulfuric acid solution with large hydrogen evolution but this treatment increases the possibility of contamination and too often, just does not work. To avoid this problem, we always used freshly prepared substrates put into the CdTe bath immediately after nickel plating. This precaution was extended later and long time exposure to air, between operations was avoided.

The most important limitation in using nickel as a substrate for CdTe solar cells is, that above 200 °C, nickel competes with cadmium for tellurium and therefore nickel telluride will form at the interface. This produces an unreliable ohmic contact and diminishes the adherency of CdTe even further. The solution should be a coat of a cadmium thin layer which can be easily electrodeposited on top of the nickel. We tried this repeatedly but were unable to get conclusive results.

BOROSILICATE GLASS

Frustated with the lack of progress on our Schottky barrier devices on nickel substrates, we switched to ITO coated Corning 7095 glass. The immediate results were the realization that the physical properties of the glass, conductive coating, cadmium sulfide and cadmium telluride fit the needs of the device structure much better than in the previously adopted structure. 3% conversion efficiency was obtained on an CdS/CdTe prepared by us in one of our first attempts. The efficiency was limited not by the electrical properties of the active layer but by the poor preparation of the window layer, which was too absorbent.

The cleanliness of the glass is very important and if lack of adherency is observed, it is entirely because of improper cleaning. We soaked the glass substrate for one hour in an alkaline cleaner. The substrate was then cleaned for 20 minutes in ultrasonic cleaner with the same but warm solution. Five minutes of vapour degreasing with methanol followed and another five minutes of ultrasonic cleaning was used.

The adherency of cadmium sulfide on ITO covered Corning 7095 glass is good. The adherency of cadmium telluride on cadmium sulfide is excellent. On ITO, cadmium telluride does not adhere as well but this is unimportant for the structure used and it only emphasizes the good match of the properties of the materials used.

1.4 THE PILOT LINE

The pilot line contains all the equipment necessary for wet processing and is installed in a "semi" clean air room. The main installation is for the electrodeposition of CdTe. A deionised water system is in place. A clean air bench with laminar flow suits the needs of the process.

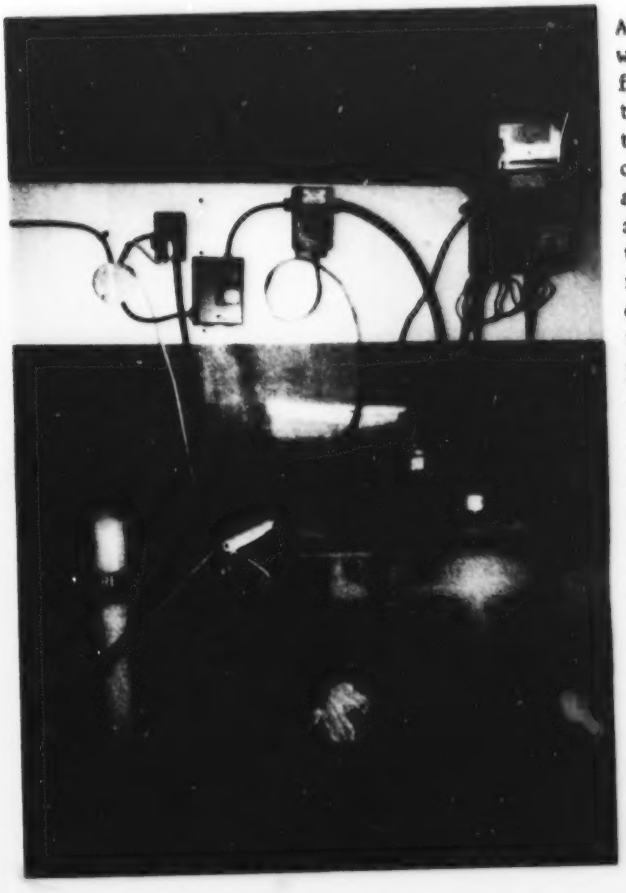


Fig. 8. The installation for the electrodeposition of CdTe

A polypropylene tank 6'x3'x3' with three compartments is fitted for cadmium and tellurium codeposition. At this time only one of the compartments is operational and has carbon electrode support bars, a quartz thermostated heater, a recirculation pump and a electrolyte agitation feature. Figure 8 is a photograph of the installation used for the electrodeposition of CdTe. It appears that three factors are critical in obtaining good CdTe on this installation:

- The purity of the deionised water used
- The inertness of the components which are in contact with the electrolyte and can produce contamination with a dramatic effect.
- The electrolyte agitation system which is responsible for the uniformity of the thickness of CdTe film.

All the components used for the construction of the plating tank were chosen carefully. Still,some of the choices which we made were wrong. We used as anodes, graphite bars (Fig 9) distributed to produce a uniform electric field in electrolyte. The bonding compound used in graphite dissolved slowly, contaminating the electrolyte. This had a disastrous effect on the quality of the CdTe deposit. It took three agonizing months until we realised this source of contamination.

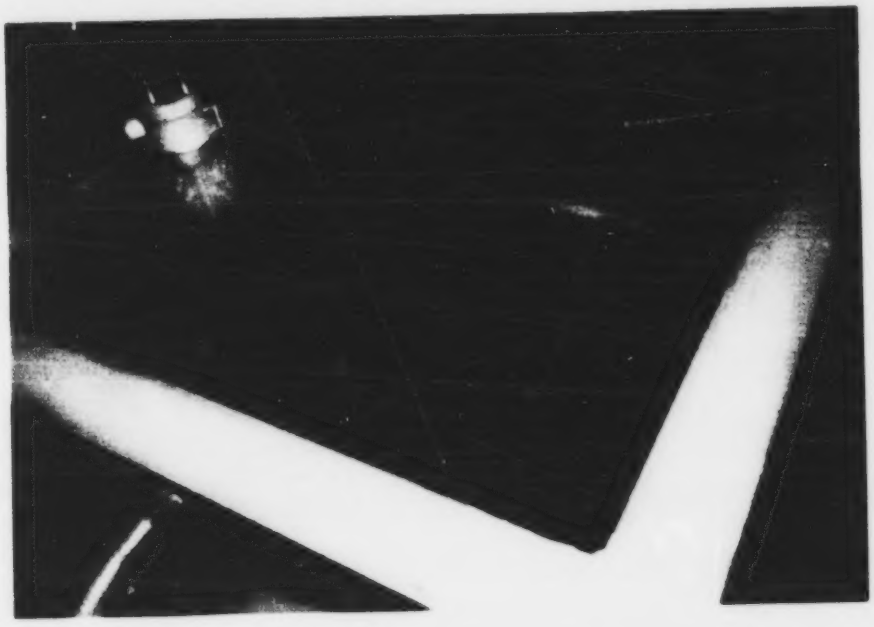


Fig. 9. Anode and electrolyte agitation construction

Polyamide screws, used in direct contact with the electrolyte decomposed slowly and are not appropriate.

The 6'x3' lead used to cover the tank was made from transparent PVC after the original acrylic lead become matted by the rather neutral electrolyte.

The filter and the pump are made from polypropylene. Flexible pipes are plasticized PVC.

D.I. WATER SYSTEM

An identical tank as that used for depositing the CdTe, and set-up as shown in figure 10, is used to supply the make-up water, replenishment and substrate rinsing. The tank has three compartments and water is pumped consecutively through a 10 inch long, polypropylene filter which retains particles as small as 0.5 microns in diameter. An activated carbon cartridge is used

to remove chlorine and organic contaminants. Finally the water passes through a dual ion exchange 0.3 cubic meter cartridge which ensures a resistivity of no more than 18 meg ohm cm. A sensor in the water line flips between a red and green light at

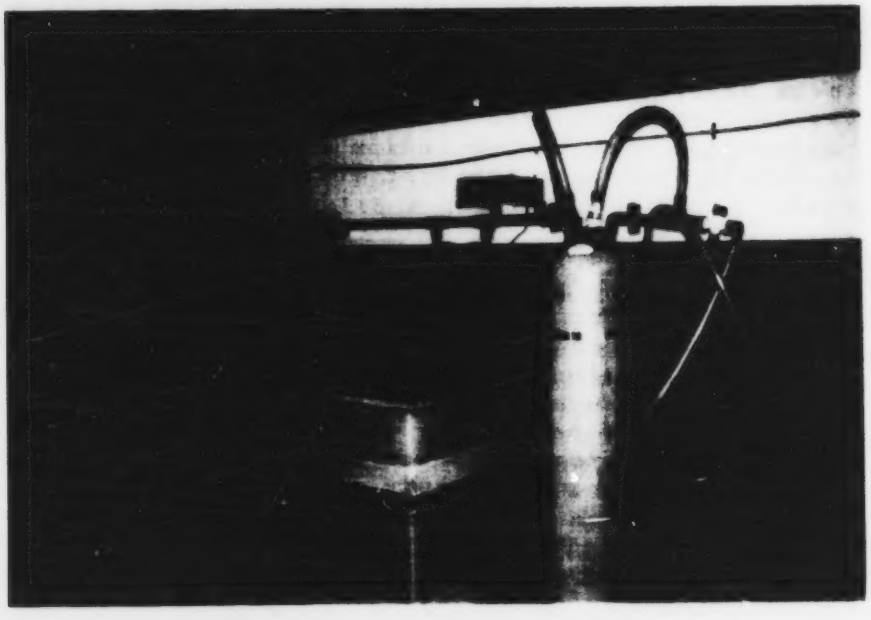


Fig. 10 D.I. water system

around 10 meg ohm cm. The water flows from one compartment to the other in such a way that even very large substrates can be rinsed properly without draining contaminants in the CdTe tank.

2. PREPARATION OF CADMIUM SULFIDE

Cadmium sulfide is an n-type semiconductor first used for solar cells fifteen years ago to produce the famous CdS/Cu2S device. This particular structure failed, with Cu2S proving to be environmentally unstable. From those early times, CdS was used more and more as window material and today, in conjunction with copper indium diselenide or cadmium telluride, produces the best performing thin film solar cells.

2.1. ELECTRODEPOSITION OF CADMIUM SULFIDE.

When this project was designed, it made good sense to try to use the same technology for the fabrication of most of the films. CdS by electrodeposition was inexpensive to produce, the waste was supposed to be minimal, and most of the "know how" learned in developing the electrodeposition of cadmium telluride was transferrable to cadmium sulfide. Unfortunately, electrodeposition of CdTe is troublesome and we did not attempt to make a high performance CdS/CdTe solar cell with both layers electrodeposited. However, all attempts to obtain a photovoltaic response from an all electrodeposited CdS/CdTe structure were successful.

Cadmium sulfide has been electrodeposited from aqueous solutions, nonaqueous organic solutions, and molten salts. Deposition from aqueous solutions have employed anodic oxidation in a sulfide containing electrolyte, and cathodic reduction from solutions containing soluble cadmium and sulfur compounds. Deposition from organic solvents have employed dimethylsulfoxide, dimethylformamide, ethylene glycol, or diethylene glycol. Deposition from fused salts have used a LiCl-KCl eutectic.

We deposited CdS from an aqueous solution containing 0.5 mole cadmium chloride, and 0.01 mole sodium thiosulfate. The current density was very low at 0.03 mA/cm square. The electrolyte was stirred and heated at 95° C. The adherency of electrodeposited CdS films on ITO coated borosilicate glass is worse than that of evaporated CdS on the same substrate heated at 200° C during deposition.

2.2. EVAPORATION OF CdS

The deposition of cadmium sulfide in a vacuum by thermal evaporation and electron beam evaporation was used at A.D. Plating on all well performing devices.

In both cases, the source material was electronic grade CdS pressed at 10,000 psi and doped with indium. The indium was added as indium sulfide with a concentration up to 0.1%.

The substrate, which was always ITO coated borosilicate glass, was kept at room temperature or heated at 200°C. For deposition made at room temperature, the films were highly absorbant and black. A 500°C annealing for 30 minutes restored the usual orange color but the absorbance was much higher than for the films deposited at 200°C.(Figure 11) The films grown at room temperature had a rather low resistivity after annealing without being doped. We used this feature when there was concern about indium diffusing in CdTe during the necessary postdeposition thermal treatments. The films grown on substrates heated at 200°C were always highly resistive if undoped. Excessive doping has detrimental effects on the junction and we still have to learn which is the optimum concentration of indium.

Fig. 11 An ITO coated glass sample with 1500 A of CdS deposited at room temperature and annealed for 30 minutes at 500C°.

The rate of evaporation was kept high at 25 Å/sec.

The adherency of films deposited on heated substrates is better than on those not heated.

3. Au/CdTe/Ni MIS SOLAR CELL.

3.1. CELL CONFIGURATION AND FABRICATION.

Large area solar cells were produced on brass substrate 86.5mmx53.0mm.

These 45.84 cm^2 brass plates were heavily plated with nickel in a sulphate-chloride bath. The nickel was glossy, amorphous and pinhole free as can be seen in figure 3.

Immediately after the electrodeposition of nickel, the substrate was introduced in the cadmium telluride bath. A glossy, black cadmium telluride film was produced in one-two hours. The film became glossy black after going through three orders of interference. The colors produced by interference on the growing film are metallic yellow, dark brown, dark blue (first order), light blue, metallic yellow, red, dark blue, (second order), green, light brown, red, blue (third order). The observation of the evolution of the interference pattern is an important tool in determining the quality of the deposition. The CdTe film is grown for a total of 4 to 10 hours for a thickness of 1-2.5 microns. The final aspect is dark grey.

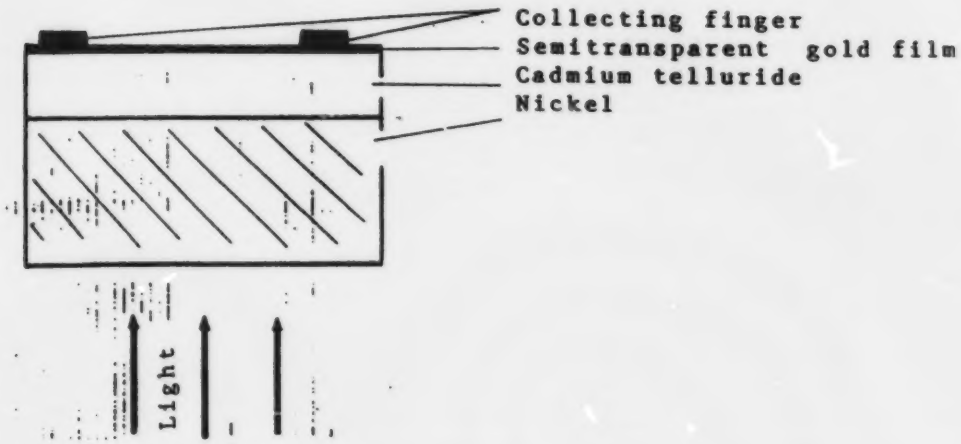


Fig. 12. MIS device structure.

The substrate with the CdTe film on it is rinsed carefully in D.I. water, blown dry with nitrogen and annealed in air at 200° C

for one hour.

Eventually a 30 A aluminium oxide layer is deposited from an electron beam heated source.

The wafer is then inserted in a holder for three consecutive metal evaporation. The first evaporation is a 100 A thick semitransparent gold layer which will produce the Schottky barrier or more likely an MIS structure . A thickness monitor is not necessary for producing a semitransparent film. If the gold source material is weighed carefully, and is evaporated completely, it will generate the same thickness film in consecutive runs.

The second evaporation will deposit the fingers and the third one the bus bar. The collection grid has to be as thick as possible and we successfully used aluminium instead of gold.

Contacting the cell is made through indium pads pressed gently on the bus bar and on the nickel substrate. Scratching the cell where gold film is present, (even the 100 A one)will short circuit the cell.

THERMAL TREATEMENT

Thermal treatment has a dramatic effect on CdTe. It can change the type from n to p. It passivates recombination centers. At 390° C the compound can recrystallize forming larger crystals with better electrical properties. Thin layers of oxide can be built by thermal treatments. Under 150° C, CdTe is very stable and no electrical behaviour changes can be produced, even with long time exposure at that temperature. Annealing in air at 200° C is a mandatory step in forming our device. Without thermal treatment, in a CdS/CdTe structure, a Voc as high as 300 mV can be observed. No more than 10 mV will be generated in an MIS structure before heat treatment.

In our opinion, this treatment homogenizes a thin layer of tellurium oxide which is formed during electrodeposition if the bath fluctuates in temperature. This layer will most likely be on the surface of the growing crystallites exposed to electrolyte and will not form inclusions. Such a mechanism of formation of the insulating layer in an MIS devices, explains the difficulties in reproducing this type of solar cell, if a good understanding of the process is not acquired.

It is easy to verify the validity of this original explanation: boiling in D.I. water for a few hours should dissolve the tellurium oxide layer. Indeed, after three hours in water at 99° C probing an CdS/CdTe device with a conductive rubber contact produced an Voc of 620 mV. Before this treatement Voc was unstable with values between 60 and 120 mV.

It is very possible that during the heat treatment in air a $CdTeO_3$ film is formed where TeO_2 does not cover the CdTe and this can be very important in defining the properties of the barrier.

The insulating 10-40 Å thick layer of oxide, if it forms during electrodeposition and during annealing, is an impossible to control parameter. Any edge or large defect in the CdTe film will trigger the nucleation of a tellurium oxide crystal if the other thermodynamic conditions are favorable. The oxide film will most likely be nonuniform and discontinuous. In its useful form, (very thin) the oxide layer can not be resolved SEM and its presence only guessed at.

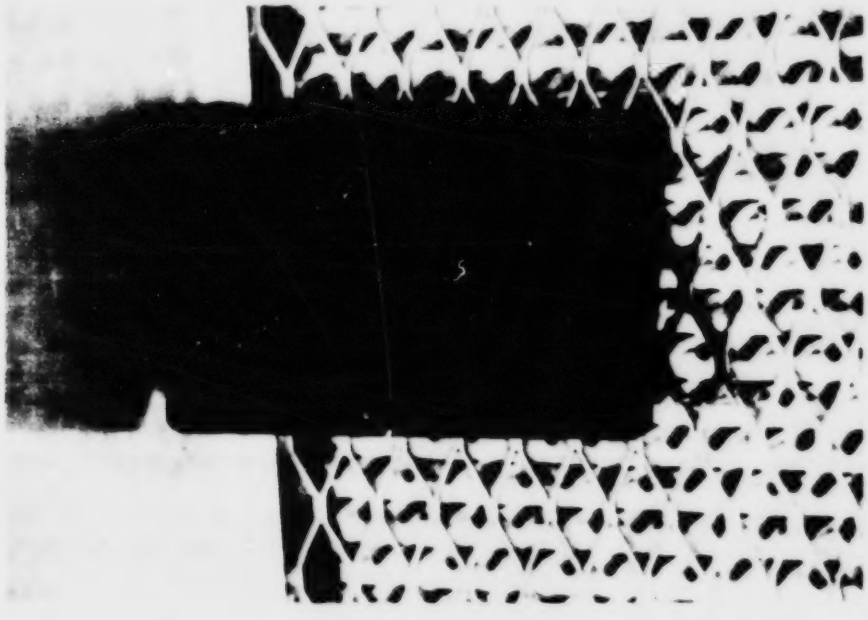


Fig. 13. Most developed large MIS device produced at A.D. Plating.

In order to obtain more reproducible MIS devices, we washed the freshly deposited cadmium telluride films carefully in a mildly alkaline solution which most likely dissolved any tellurium oxide. Then, by electron beam evaporation, 30 A of the aluminium oxide and a semitransparent gold film was evaporated. Cells obtained in this way had their performances slightly improved but nothing conclusive happened.

THE METAL CONTACT.

Built on nickel substrate, a Scottky or MIS CdTe solar cell, has to receive the imput radiation through a semitransparent

metallic coat. If CdTe is n-type, the metal has to have a high work function and we chose gold. There are three problems associated with a metallic semitransparent coat: the sheet resistivity is high; the reflection losses are high; and the spurious absorption is high.

The resistive power-loss effects are: the loss due to lateral current flow in the top metallic layer; the loss due the series resistance of the fingers and the contact resistance between the metallic substrate and cadmium telluride.

To evaluate the series resistance of the device, the collector was deposited on glass. First the semitransparent gold, then the gold fingers, and then the aluminium bust bar. The resistance from the first to the last finger was 110 ohms (bust bar not deposited). The bust bar had a resistance of 5 to 10 ohms depending on its thickness.

The geometry of the collecting grid has a dramatic effect on how much power can be collected from the device. Figure 14 shows the variations of Isc and Voc if the top collecting point was set on different fingers with the bust bar not attached. The behaviour of Isc can be explained by the increased power loss due to lateral current flow when current is collected at the edge. The behaviour of Voc is due to rather low shunt resistance.

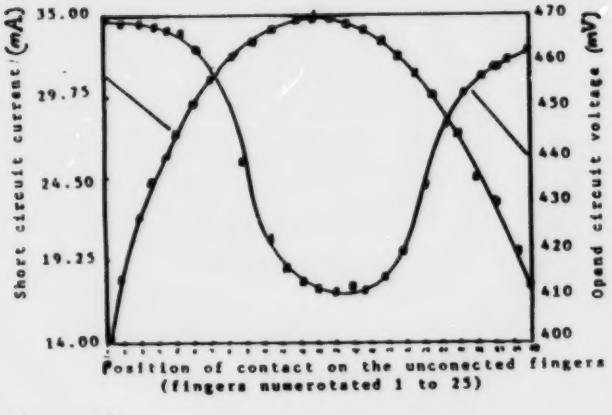


Fig. 14. Isc and Voc vs position of top contact.

The fractional power loss at the maximum power point due to lateral current flow,can be expressed as:

With =40 / . Imp=1mA/cm sq. Vmp=400 mV and S=5 mm (S is the distance between two fingers), the power loss is less than 1%. The power loss in the bust-bar (R=5 ohms) is approximately 0.3 mW and represent less than 5 % of the output power. However, if we define four cells on the same substrate, connected in parallel, the power output is three times larger than for one cell covering the whole surface. The calculated power loss considering only the series resistance does not match the experimental findings and it seems that electric shorts due to impurities, precipitates or inclusions in the deposit are uniformly distributed throughout the sample and lowers substantially the shunt resistance.

3.2 DEVICE EVALUATION

The light I-V characteristics of the solar cell pictured in figure 13 is represented in figure 15.

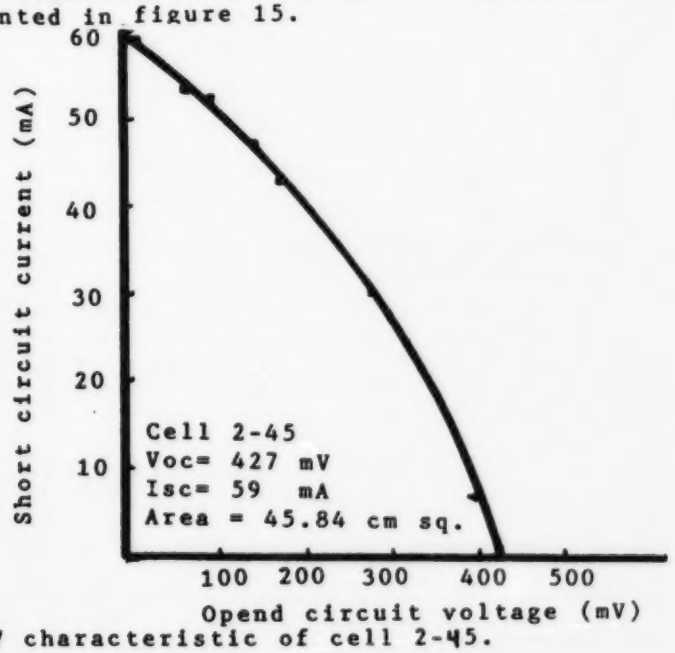


Fig. 15. Light I-V characteristic of cell 2-45.

The I-V was traced in our laboratory, using an ELH lamp inserted in the focal point of a large parabolic reflector which produces a 250 cm^2 light spot of uniform intensity. A single crystal silicon reference cell, which gives 148 mA if illuminated with 100 mW/cm^2, was used to calibrate the solar simulator. The spectral response of the reference and test cells are not very similar but for now, when we are not chasing state-of-the-art performance, the accuracy is satisfactory. Black gloves were used to manipulate cells under testing. The temperature of the cells was between 20° and 23° C. A four points contacting scheme was used to eliminate effects due to series resistance of the test leads and associated contact resistance.

Parallel to our testing, we tested some of our films and devices at Ametek-Applied Materials to confirm our measurements and procedures. Months ago, Ametek was setting records on CdTe solar cells but the R&D operation was closed down recently despite strong government support and appreciation.

The results of measurements done at Ametek are summarised in table 1 and table 2. For films annealed at 200°C, our devices behaved much better than those processed at Ametek considering the large area of our cells and Ametek's processing which included two extra steps.

Table 1. Characteristics of MIS devices produced on films annealed at 200° C. (Measured at Ametek)

Area 0.08 cm^2

1) Eff: 0.716	Voc: 0.577	Jsc: 5.12 mA/sq. cm.	
FF: 24.2	Rs: 18.0 ohms.cm sq.	Isc: 0.409 mA	
2) Eff: 0.774	Voc: 0.570	Jsc: 5.39 mA/sq. cm.	
FF: 25.1	Rs: 14.2 ohms.cm sq.	Isc: 0.431 mA	
3) Eff: 0.682	Voc: 0.564	Jsc: 4.96 mA/sq. cm.	
FF: 24.3	Rs: 16.3 ohms.cm sq.	Isc: 0.397 mA	
4) Eff: 0.736	Voc: 0.574	Jsc: 5.28 mA/sq. cm.	
FF: 24.2	Rs: 17.2 ohms.cm sq.	Isc: 0.422 mA	

Average of 4 cells:

Eff: 0.727(+/-0.03)% Voc: 571(+/-5.61)mV
FF: 24.4(+/-0.45) Jsc: 5.19(+/-0.18)mA/cm sq.

45 cm^2 cell(three measurements on the same sample):

Eff: 0.139	Voc: 0.081	Jsc: 6.87 mA/sq. cm.	
FF: 24.9	Rs: 1.17 ohms.cm sq.	Isc: 309 mA	
Eff: 0.140	Voc: 0.079	Jsc: 6.87 mA/sq. cm.	
FF: 25.5	Rs: 1.13 ohms.cm sq.	Isc: 309 mA	
Eff: 0.137	Voc: 0.794	Jsc: 7.01 mA/sq. cm.	
FF: 24.4	Rs: 1.16 ohms.cm sq.	Isc: 309 mA	

Table 2. Characteristics of MIS devices produced on films annealed at 300° C. (Measured at Ametek)

Area 0.08 cm^2

1) Eff: 1.69	Voc: 0.649	Jsc: 8.39 mA/sq. cm.	
FF: 31.1	Rs: 24.7 ohms.cm sq.	Isc: 0.684 mA	
2) Eff: 1.83	Voc: 0.624	Jsc: 8.73 mA/sq. cm.	
FF: 33.5	Rs: 23.2 ohms.cm sq.	Isc: 0.698 mA	
3) Eff: 1.75	Voc: 0.637	Jsc: 8.55 mA/sq. cm.	
FF: 32.0	Rs: 31.3 ohms.cm sq.	Isc: 0.684 mA	
4) Eff: 1.88	Voc: 0.617	Jsc: 8.98 mA/sq. cm.	
FF: 33.8	Rs: 16.6 ohms.cm sq.	Isc: 0.718 mA	
5) Eff: 1.81	Voc: 0.624	Jsc: 8.67 mA/sq. cm.	
FF: 33.5	Rs: 18.8 ohms.cm sq.	Isc: 0.694 mA	

Average of 5 cells:

Eff: 1.79(+/-0.07)% Voc: 0.630(+/-12.7)mV
FF: 32.8(+/-1.18) Jsc: 8.66(+/-0.21)mA/cm^2

For the films annealed at 300° C, it was supprising to see efficiencies three times better than for films annealed at 200° C. It is our understanding that at 220° C nickel telluride forms with bad effects on the back contacts. Furthermore, over 220° C CdTe films dust off.

Ametek heated our films at 300° C. Most of the films dusted off as expected, but where this did not happen, efficiency as in table 2 was obtained. It is far less than we believe it can be, but with cost of a few cents / 100 cm^2 of cell there is commercial application.

4. CdTe/CdS SOLAR CELL

4.1. DEVICE FABRICATION

On borosilicate glass Corning 7095, ITO coated, 1000-1500 Å of cadmium sulfide is deposited as discussed in 2.2.

The glass, with ITO and CdS on it, is rinsed in D.I. water, attached to a platinum holder and introduced in the plating tank for CdTe electrodeposition. One-two and a half microns of CdTe is deposited.

The "sandwich" is rinsed, then dipped in a saturated solution of CdCl in methanol at 25 degrees Celsius. It is blown dry (unrinsed) with nitrogen, rinsed, and annealed at 390 C for thirty minutes.

After annealing, the wafer is rinsed carefully,etched for 10 seconds in 0.01 % bromine in methanol and rinsed again carefully. It is blown dry and immediately introduced in a vacuum system for gold evaporation. A consecutive annealing at 150 C for 30 minutes is used to improve the back contact.

The wafers are 3"x3" and are pictured in figure 16 and 17.

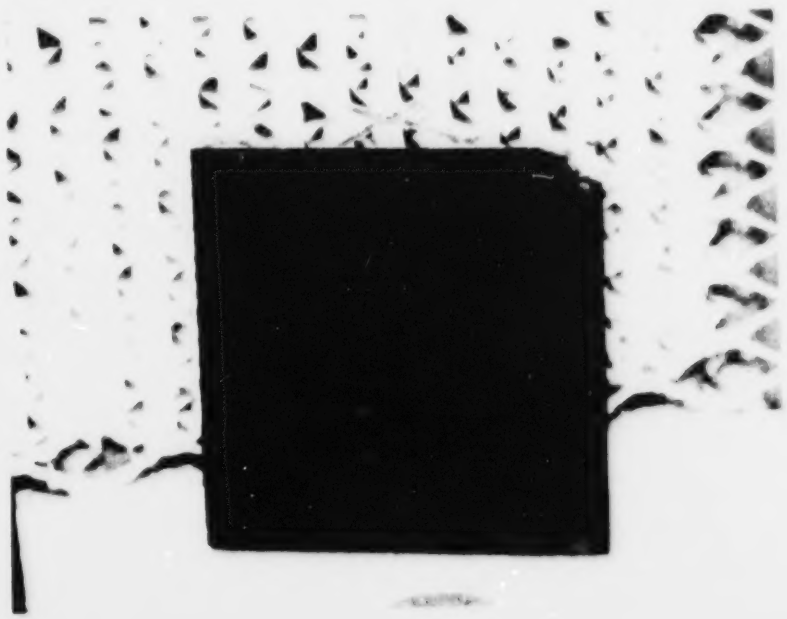


Fig. 16 An 3"x3" wafer with CdS and CdTe seen from the front.

As can be seen in figure 17, the gold is evaporated through two consecutive masks. First rectangles 0.5x0.6 cm are defined. Then, once all the 33 cm^2 cells are tested, a new layer of

gold is deposited to define a larger device.

THERMAL TREATMENTS.

In the case of MIS devices, the thermal treatments role was to release some of the tension in the film to improve crystallinity and to generate a thin layer of oxide.

In the case of CdS/CdTe, depending on what structure is desired, the thermal and chemical treatments are used to manipulate the type and resistivity of cadmium telluride and the quality of the films.

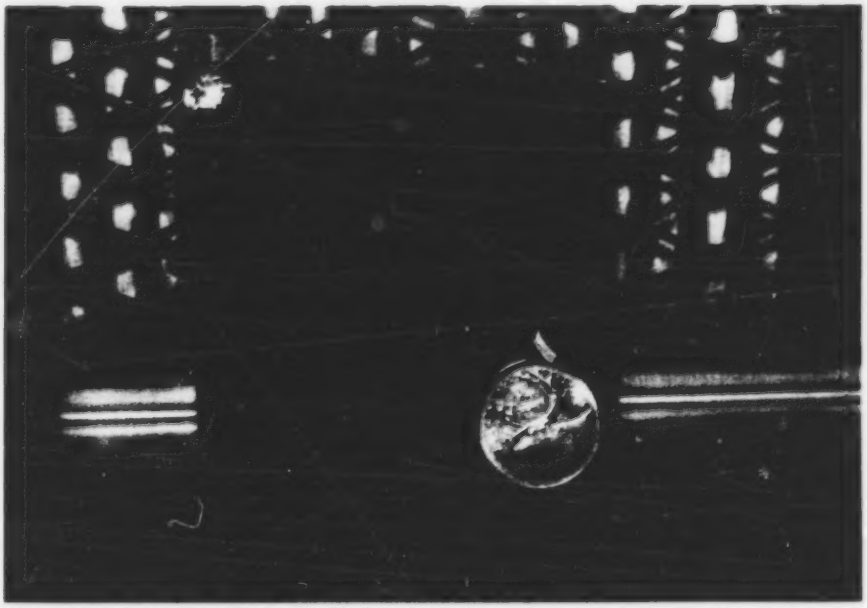


FIG. 17. A wafer with 5x6 mm sq. cells viewed from the back.

The configuration alone is not sufficient to produce high efficiency CdS/CdTe solar cell. Subtle changes in the process has a significant effect on device properties. Some of the changes are accidental and unaccounted for, making some of the results unexpected. However, the flexibility and design possibilities of this structure are outstanding.

There are two structures which produced above 10 % efficiency solar cell; a p-n heterojunction and a n-i-p device. The n-p cell is produced by heating the package of CdTe/CdS/ITO/glass at 390 C. We Then etch and contact the p-type CdTe with gold. The n-i-p device is produced in the same way but the back contact is improved by replacing gold with heavily doped p-type ZnTe. The band diagram of the two structures are presented in figure 18 and 19. It is debatable whether the n-i-p device is that much different with so little change in process. Recently four research

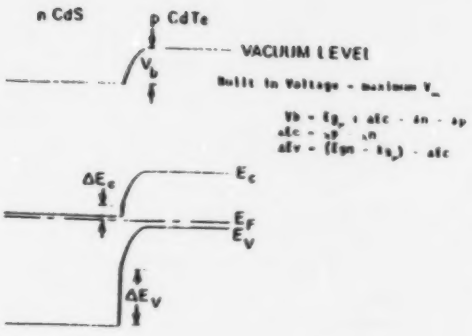


Fig. 18. Idealized band diagrame of the CdS/CdTe/Au n-p solar cell.

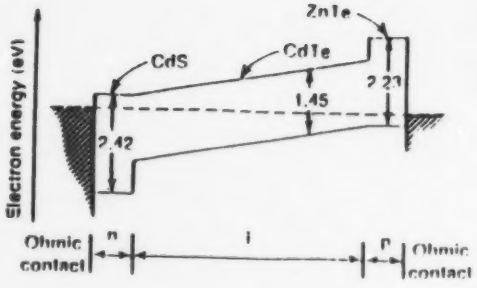


Fig. 19. Idealized band diagrame for the CdS/CdTe/ZnTe n-i-p solar cell.

laboratories independently concluded that the CdS/CdTe/ZnTe is indeed an n-i-p structure.

SPECTRAL RESPONSE

The spectral response of a solar cell is the output current under short circuit, per unit incident power, in monocromatic light as a function of wavelength.

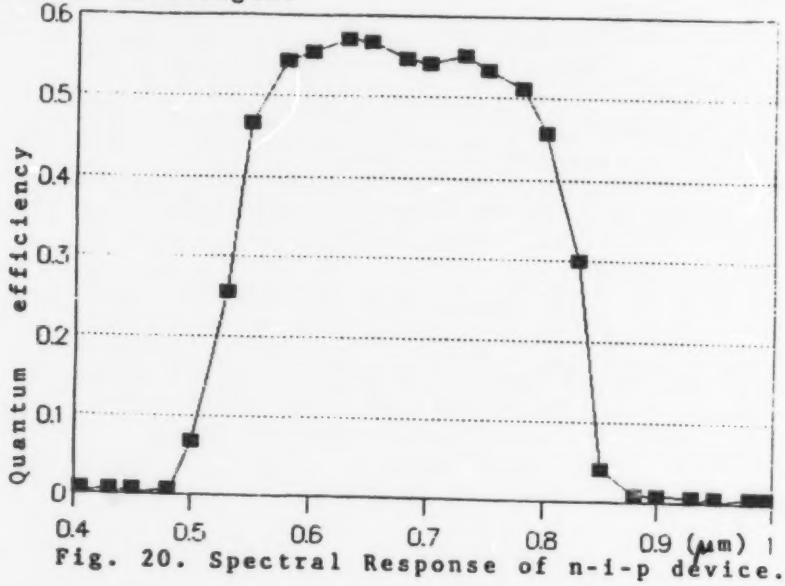


Fig. 20. Spectral Response of n-i-p device.

The spectral response of an n-i-p device fabricated on a CdS/CdTe wafer, produced at A.D. Plating, is shown in figure 20. The quantum efficiency is relatively low only due to absorption in the thick CdS. Otherwise, Isc is strong over a wide region which suggests a very good quality CdTe, with the junction situated at the CdS/CdTe interface. If the junction were situated deeper in the absorber, the short wave radiation would not

produce a strong respose. If the quality of CdTe were debatable, the long wave radiation which penetrate further would generate carriers which will recombine before reaching the junction and so the response, in this part of the spectrum, would be weak.

LIGHT I-V

Our best cell to date has an efficiency of 5.46% and has the characteristics as shown in figure 21. A 8.8 % device was produced and measured but the short circuit current density was at 32 mA/cm^2. This current density is 4 mA/cm^2 over the record of 28 mA/cm^2 and it is possible that this cell collected, generated minority carriers from an area substantially larger than defined by the gold back contact. When we tried to detach this cell by scratching around the gold contact, we touched the gold and, as always, the cell was shorted.

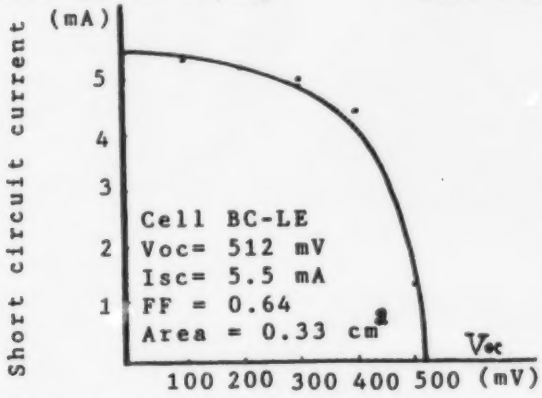


Fig 21. Light I-V characteristic of cell BC-LE

On films fabricated at A.D. Plating, n-p and n-i-p devices were defined and measured at Ametek and the results are tabulated in table 3 and 4. The CdS was intentionally much thicker than optimum (to eliminate doubts about the source of limitations) and the efficiencies would be at least twice as high if CdS was half as thick.

Table 3. Characteristics of n-p CdS/CdTe devices
Area 0.08 cm^2.

Eff: 2.12	Voc: 0.380	Jsc: 11.6 mA/cm^2
FF:47.9	Rs: 1.03 ohms cm^2	Isc: 0.929 mA
Eff: 1.94	Voc: 0.384	Jsc: 11.1 mA/cm^2
FF:45.5	Rs: 1.21 ohms cm^2	Isc: 0.888 mA
Eff: 1.80	Voc: 0.364	Jsc: 11.3 mA/cm^2
FF:43.5	Rs: 1.23 ohms cm^2	Isc: 0.909 mA
Eff: 1.82	Voc: 0.381	Jsc: 10.9 mA/cm^2
FF:43.8	Rs: 1.36 ohms cm^2	Isc: 0.872 mA
Eff: 2.04	Voc: 0.401	Jsc: 11.9 mA/cm^2
FF:42.3	Rs: 1.46 ohms cm^2	Isc: 0.958 mA

Average of 5 cells

Eff: 1.94(+/-0.13)% Voc: 382(+/-13.1)mV Jsc: 11.3 mA/cm^2
FF: 44.6(+/-2.17) Rs: 1.25(+/-0.16)ohms cm^2

Table 4. Characteristics of n-i-p CdS/CdTe/ZnTe devices
Area 0.08 cm^2

Eff: 3.10	Voc: 0.590	Jsc: 10/9 mA/cm^2
FF:47.8	Rs: 1.95 ohms cm^2	Isc: 0.877 mA
Eff: 2.82	Voc: 0.578	Jsc: 9.57 mA/cm^2
FF:51.3	Rs: 1.48 ohms cm^2	Isc: 0.7.65mA
Eff: 2.67	Voc: 0.556	Jsc: 9.43mA/cm^2
FF:50.7	Rs: 1.49 ohms cm^2	Isc: 0.754 mA
Eff: 2.65	Voc: 0.565	Jsc: 9.98mA/cm^2
FF:47.1	Rs: 1.78 ohms cm^2	Isc: 0.798 mA
Eff: 2.74	Voc: 0.576	Jsc: 10.0 mA/cm^2
FF:47.5	Rs: 1.95 ohms cm^2	Isc: 0.801 mA
Eff: 2.96	Voc: 0.573	Jsc: 10.5 mA/cm^2
FF:48.9	Rs: 1.64 ohms cm^2	Isc: 0.844 mA
Eff: 2.72	Voc: 0.567	Jsc: 9.88mA/cm^2
FF:48.5	Rs: 1.74 ohms cm^2	Isc: 0.790 mA

Average of 7 cells:

Eff: 2.81	Voc: 0.572V	Jsc: 10.0 mA/cm^2
FF:48.8	Rs: 1.71 ohms cm^2	

5. CONCLUSIONS.

Over the last two years A. D. Plating has gained substantial experience in making CdTe based polycrystalline solar cells.

A pilot station for the electrodeposition of CdTe was built. We were able to produce on this pilot station, with industrial grade chemicals, a 5.5 % efficiency CdS/CdTe device and 2% efficiency MIS device.

While the polycrystalline thin film solar cell has become the leader in solar energy conversion for terrestrial application, A.D. Plating is one to two years away from commercial production of this type of solar cell.

The process is difficult. Subtle changes in preparation have dramatic effect on performances. The most difficult time in learning to produce thin film polycrystalline solar cells has passed, but one or two years of R&D work is still necessary to improve the yield, to increase the efficiency, and to produce submodules.

6. RECOMMENDATION.

Despite the fact that we missjudged the difficulty of the project, the work has to be finalized.

In situ purification of the chemicals has to be improved. Better yield will result.

Experimental production on MIS devices, even at efficiency of 2%, should be started and sustained by marketing such solar cells in novelty gadgets and science kits.

A.D. Plating should enter the race for record high performance of CdS/CdTe solar cells.

Submodule CdS/CdTe has to be designed and fabricated.

Equipment for CdS deposition and for back contact metalization has to be designed and built to match the output of the electrodeposition pilot station.

The "one man band" aproach in which we were forced by financial restraint, has to be changed and, with some government support we can do that.

ANNEX 1

ELECTRODEPOSITION OF CdTe. THEORETICAL

The most used method for obtaining CdTe by electrodeposition is the cathodic codeposition of individual components with the formation of the compound on the cathode.

For an electrolyte containing Cd^{2+} and Te^{4+} ions in an acid aqueous solution, the cathode reactions and corresponding equilibrium electrode potentials are

(1) $Cd = Cd^{2+} + 2e^{-}$,

(2) $E_{Cd} = E^{o}_{Cd} + \frac{RT}{2F} \ln(a_{Cd^{2+}}/a_{Cd}) = -0.403 + 0.0295 \log (a_{Cd^{2+}}/a_{Cd})$

(3) $Te + 2H_2O = HTeO_2^{+} + 3H^{+} + 4e^{-}$ $(0 < pH < 5)$,

(4) $E_{Te} = E^{o}_{Te} + \frac{RT}{4F} \ln (a_{HTeO_2^{+}}/a_{Te}) + \frac{3RT}{4F} \ln C_{H^{+}} =$

$= 0.551 + 0.148 \log (a_{HTeO_2^{+}}/a_{Te}) - 0.0443\ pH$.

It is useful to introduce a quasi rest potential defined as the potential of the deposit relative to the electrolyte with activities of potential determining species as they are at the solid -electrolyte interface during deposition.

This quasi rest potential arises from the interplay of the equilibrum potential of the components, their interaction forming CdTe, the value of the activities of Cd^{2+} and Te^{4+} in the electrolyte at the interface solid-electrolyte during

deposition and from the relative magnitude of exchange currents in the deposit.

CdTe has an existence range stretching from CdTe in equilibrium with Cd to CdTe in equilibrium with Te . The activities are related by

(5) (6)

$$\frac{a_{CdTe}}{a_{Cd}\,a_{Te}} = \exp(-G_{CdTe}/RT) \quad \text{or for } a_{CdTe}=1 \quad a_{Cd}\,a_{Te} = \exp(G_{CdTe}/RT)$$

At CdTe/Te boundry , $a_{Cd} = \exp(G_{CdTe}/RT)$,

and $a_{Cd} = 1$ at CdTe/Cd boundry.

An opposite variation will occur for a_{Te}.

At 25 °C, one mole of Te reacting with one mole of Cd liberates 25.5 kcal and this value of the enthalpy of formation is a good measure of the increment in the Gibbs free energy.

As a result of compound formation the Cd potential shifts from the standard value of - 0.403 V at the CdTe/Cd boundry, to $-0.403+G_{CdTe}/2F = -0.403+0.546 = 0.143$ V at the CdTe/Te phase boundry.

The tellurium potential jump from the standard value of 0.551V at the CdTe/Te phase boundary to $0.551 + G_{CdTe}/4F =$ 0.824 V at the CdTe/Cd boundary.

Since a deposit of one composition can have only one quasi rest potential, it is possible to deposit Cd and Te in stochiometric amounts only if we can make

$$(7) \quad E_{CdTe} = E_{Cd} = E_{Te} ,$$

This can be done by using an electrolyte with a high concentration of the less noble component Cd and a low concentration of the noble component Te which can be show as follows :

From eq.(2), (4) and (7),

$$(8) \quad \frac{RT}{F} \ln (a_{Cd}^{1/2} / a_{Te}^{1/4}) = (E_{Te}^{o} - E_{Cd}^{o}) + \frac{RT}{F} \ln (a_{Cd}^{1/2} / a_{Te}^{1/4})$$

At CdTe/Cd boundary:

$$(9) \quad \frac{RT}{F} \ln (a_{Cd}^{1/2} / a_{Te}^{1/4}) = E_{Te}^{o} - E_{Cd}^{o} = \frac{G}{4F}$$

At CdTe/Te phase boundary:

$$(10) \quad \frac{RT}{F} \ln (a_{Cd}^{1/2} / a_{Te}^{1/4}) = E_{Te}^{o} - E_{Cd}^{o} + G/2F .$$

Using $G/2F = 0.546$ V and

$$E_{Te}^{o} - E_{Cd}^{o} = 0.551 + 0.403 = 0.594 \text{ V}$$

condition (9) and (10) can be satisfied only if

$$(12) \quad a_{Te}^{4+} << a_{Cd}^{2+} .$$

From a practical point of view, at sufficiently low concentrations of Te^{4+} ions the rate of deposition becomes

diffusion controlled and we can increase the deposition voltage until Cd will deposit. Cd deposition will occur at a potential less negative than E_{o}^{Cd} by using the increment in Gibbs free energy when CdTe forms.

It should be pointed out that in the above considerations the rate constants of the exchange current were considered widely different with Cd the potential determining specie. This condition can be questioned in view of some of our experiments in which we were not able to obtain reliable n-type CdTe films . Even at a voltage above E_{o}, the Cd film or crystallites were covered with a dark pelicule resembling CdTe.